

# PATENT ABSTRACTS OF JAPAN

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## (54) WEAKLY ACIDIC CATION EXCHANGE MEMBER

### (57)Abstract:

PURPOSE: To prevent omission of weakly acidic ion exchange material from a porous carrier by coating the surface of the porous carrier with a weakly acidic cation exchange compsn., comprising a copolymer crosslinked material of vinyl compd. with unsatd. carboxylic acid and/or unsatd. carboxylic acid diene monomer copolymers.

CONSTITUTION: Copolymers of unsatd. carboxylic acid (e.g. maleic acid anhydride) and/or unsatd. carboxylic acid diene monomers are dissolved with a vinyl compd. having hydrophobic groups selected from alkyl groups, aryl groups, and aralkyl groups of  $\geq 3$  carbon number in a solvent such as methanol with a polymn. initiator (e.g. benzoyl peroxide). A porous carrier such as silica gel or the like is added to this liquid, which is then concentrated for the reaction to coat the surface of the porous carrier with the copolymer crosslinked material at high density. Thereby, omission of the weakly acidic ion exchange material from the porous carrier can be prevented. Also, the rate of elution of bivalent cations can be increased, which enables simultaneous analysis of ultramminute amt. of univalent and bivalent cations.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the weak acidic cation exchanger used for the liquid chromatography which an isolation column is filled up and can measure a univalent and divalent positive ion simultaneously about a weak acidic cation exchanger.

[0002]

[Description of the Prior Art] Conventionally, the liquid chromatography which measures a univalent and divalent positive ion introduces a sulfone group into polymer gel, or the highly acidic cation exchanger which carried out the chemical bond of the propyl sulfone group to silica gel has been used widely. However, since eluate conditions completely differed, it was impossible to have measured a univalent and divalent positive ion simultaneously in the highly acidic ionic exchanger of these. This is clear from compendiums, such as a high-performance-chromatography handbook which the Japan Society for Analytical Chemistry edited.

[0003] In recent years as a weak acidic cation exchanger which solved this problem The particle diameter of 5 micrometers, To the silica gel surface of the pore diameter of 10 nm, and surface area <sup>2</sup>[ of 380 m ]/g. After forming the tunic of the polybutadiene maleic acid (mole ratio 1 to 1) containing 4% of JIKYU mill peroxide, the weak acidic cation exchanger which was heated for 4 hours and manufactured at 180 \*\* was announced (Chromatographia, Vol.23, No.7, P465 -472 reference). Although the univalent and divalent positive ion was simultaneously measured with the liquid chromatography using this weak acidic cation exchanger by making into an eluate the organic acid which is weak acid, When performing liquid chromatography as a device which furthermore improves this method using the same cation exchanger, By adding pyridine- 2,6-dicarboxylic acid and making complex salt with a divalent positive ion form into an eluate, the retention volume ratio of a divalent positive ion. (k' shows hereafter.) -- the method of making it decrease selectively and shortening measuring time was announced (Am.Lab. (Fairfield Conn.) Vol.21, No.5, P92 -101 reference).

[0004]

[Problem(s) to be Solved by the Invention] However, when filling up a column with the weak acidic cation exchanger manufactured by the method of the above-mentioned report, It was difficult to manufacture the packed column using the weak acidic cation exchanger which has the problem that the polybutadiene maleic acid covered to the silica gel surface is easily missing from silica gel support and in which it had the stable ion exchange capacity. In liquid chromatography, there was also troublesomeness of adjusting the selectivity of a univalent and divalent positive ion, by adding a special reagent called pyridine- 2,6-dicarboxylic acid to an eluate.

[0005] The purpose of this invention makes the polymer tunic which carried out copolymerization bridge construction with high density on the surface of the porous carrier form, and prevents lack of a weak acidic cation-exchange constituent, And the eluate which added a special reagent like pyridine- 2,6-dicarboxylic acid is not needed, but it is in providing a disengageable weak acidic cation exchanger simultaneously about univalent and a divalent positive ion.

[0006]

[Means for Solving the Problem] A result of having advanced research wholeheartedly in order that this invention persons might attain the above-mentioned purpose, By making a weak acidic cation exchanger constituent which consists of a copolymerization bridging body of unsaturated carboxylic acid and/or an unsaturated-carboxylic-acid diene MOMA copolymer, and a vinyl compound cover with high density on the surface of a porous carrier, it found out that said problem could be canceled.

[0007] That is, this invention is in a weak acidic cation exchanger which has covered a weak acidic cation-exchange constituent which comprises a copolymerization bridging body of unsaturated carboxylic acid and/or an unsaturated-carboxylic-acid diene monomer copolymer, and a vinyl compound on the surface of a porous carrier. This invention is the aforementioned weak acidic cation exchanger, and a vinyl compound which is the component is in a weak acidic cation exchanger which has a with a carbon numbers of three or more alkyl group, an aryl group, and the hydrophobic group chosen from a group which consists of aralkyl groups.

[0008] This invention is explained in full detail below. Weakly acidic cation exchange resin of this invention is obtained by a following method. After first dissolving unsaturated carboxylic acid and/or an unsaturated-carboxylic-acid diene monomer copolymer, one or more sorts of vinyl compounds, and a radical polymerization initiator by organic solvents, such as methanol or acetone, you add a porous carrier and make it suspended uniformly. And a tunic which carries out vacuum concentration by a rotating evaporator etc., and serves as a

weak acidic cation-exchange constituent on the porous carrier surface is formed. Next, after it puts the above-mentioned porous carrier film formation thing which carried out vacuum concentration into the inside of a container which can be heated, for example, a vacuum drier, and inactive gas, for example, nitrogen gas, replaces, a weak acidic cation exchanger of the invention in this application can be manufactured by heat-treating.

[0009]In a weak acidic cation exchanger of the invention in this application, a maleic anhydride, maleic acid, fumaric acid, itaconic acid anhydride, itaconic acid, acrylic acid, etc. are mentioned as unsaturated carboxylic acid to be used.

[0010]As an unsaturated-carboxylic-acid diene monomer copolymer, a copolymer of the above-mentioned unsaturated carboxylic acid and a diene monomer chosen from butadiene, isoprene, chloroprene, etc. is used. A mole ratio at the time of polymerizing these has a desirable thing of the range of 90/10 to 30/70 at unsaturated carboxylic acid/diene monomer.

[0011]Aforementioned unsaturated carboxylic acid and an unsaturated-carboxylic-acid diene monomer copolymer may use either independently, and may use it combining both. However, 50 copies are required for these total amounts from five copies to 100 copies of porous carriers. It is the range of 15 to 40 copies preferably.

[0012]In a weak acidic cation exchanger of the invention in this application, although there are a polyvinyl compound and a monovinyl compound as a vinyl compound, a polyvinyl compound may be used independently and may be used together with a monovinyl compound.

[0013]As a polyvinyl compound, it is polybutadiene (the range of 300 to 10000), for example. [ a molecular weight ] An average molecular weight preferably A thing of 1000 to 5000, pentaerythritol tetraacrylate, Diacrylate and dimethacrylate, such as trimethylolpropanetrimethacrylate, ethylene glycol, and a polyethylene glycol, Oligomer (thing of the range of a dimer to the molecular weight 10000) of divinylbenzene, triallyl isocyanurate, triaryl cyanurate, diallyl phthalate, triallyl trimellitate, glycerol dimethacrylate, and these polyvinyl compound, etc. are mentioned.

[0014]As a monovinyl compound, acrylic acid alkyl ester (alkyl: thing more than  $C_3H_7$ ), Methacrylic acid alkyl ester (alkyl: thing more than  $C_3H_7$ ), acrylic acid cyclohexyl, benzyl methacrylate, styrene, alpha-methylstyrene, vinyltoluene, ethylvinylbenzene, dimethylstyrene, etc. are mentioned.

[0015]independent in a vinyl compound which has a with a carbon numbers of three or more alkyl group, an aryl group, and one or more hydrophobic groups chosen from an aralkyl group, in order to give hydrophobicity to a weak acidic cation-exchange constituent -- or more than one can be used.

[0016]That, as for, vinyl compounds, such as trichloro vinylsilane and vinyl alkoxysilane, carried out the chemical bond to a porous carrier directly has the work which makes many weak acidic cation-exchange constituents on the porous carrier surface support.

[0017]As for these vinyl compounds, it is desirable to total at least one or more sorts to 100 copies of porous carriers, and to add 40 copies from one copy, and they are good to add 30 copies from one copy especially. Acrylic acid alkyl ester (thing more than  $C_4H_9$ ), acrylic acid cyclohexyl, methacrylic acid alkyl ester (thing more than  $C_4H_9$ ), especially a vinyl aryl compound, etc. are preferred among vinyl compounds with a hydrophobic group.

[0018]As a radical polymerization initiator, peroxide system polymerization initiators, such as azobis system polymerization initiators, such as 2,2, - azobisisobutyronitrile, 2, 2, - azobis (2,4-dimethylvaleronitrile), benzoyl peroxide, lauroyl peroxide, are desirable, for example.

[0019]Polystyrene gel etc. which are organic porous carriers, such as silica gel, alumina, porous glass, a carbon grain, etc. which are inorganic porous carriers as a porous carrier, are contained, and thing of particle diameter of the range of 3 to 50 nm is [ 1 micrometer to 30 micrometers, and a pole diameter ] desirable.

[0020]In the above-mentioned manufacturing method, cooking temperature heat-treatment conditions From 100 \*\* to 200 \*\*. It can be desirably considered as 150 to 180 \*\*, and the cooking time can cover enough vinyl copolymerization bridge construction constituents with high density on the porous carrier surface by considering it as the range of 3 to 7 hours desirably from 2 hours for 10 hours.

[0021]

[Example]Below a typical example is shown and the invention in this application is explained to it still more concretely. These are mere illustration for explanation and it cannot be overemphasized that this invention is not what is restricted to these in any way.

[0022]4.0 g of example 1 polybutadiene maleic acid (the mole ratio of butadiene/maleic acid may be 1/1 hereafter.), 0.16 g of JIKYU mill peroxide was mixed with 0.5g of triallyl isocyanurate, and 0.5 g of vinyltoluene in a 300-ml eggplant type flask as a polymerization initiator as a vinyl compound, 150 ml of methanol was added, and it dissolved thoroughly. Subsequently, after adding the silica gel 10g of the particle diameter of 5 micrometers, the pole diameter of 10 nm, and surface area <sup>2</sup>[ of 350 m ]/g and making it suspended uniformly, it condensed making it rotate by 45 \*\* and 650mmHg using a rotating evaporator, and the tunic was formed in the silica gel surface. After silica gel in which the tunic was formed moved only the sieve part opium poppy and the powder portion into the vacuum drier using the sieve made from stainless steel of 200 meshes and made them a nitrogen gas atmosphere, it was heated at 180 \*\* for 4 hours, and manufactured the weak acidic cation exchanger.

[0023]After methanol washes the obtained weak acidic cation exchanger, fill up the isolation column for liquid

chromatography and Two kinds of eluates, That is, the sample was separated using eluate A:7.5mM citrate / 0.75mM pyridine- 2,6-dicarboxylic acid solution, and an eluate B:3mM nitric acid solution. The measured sample did 30microl pouring of this with the mixed solution of the concentration of  $\text{Li}^+$ :2 mg/l,  $\text{Na}^+$ :10 mg/l,  $\text{NH}_4^+$ :10 mg/l,  $\text{K}^+$ :20 mg/l,  $\text{Mg}^{2+}$ :10 mg/l, and  $\text{Ca}^{2+}$ :20 mg/l. The conductivity detector was used for detection.

[0024]The chromatogram obtained by the eluate B was shown in drawing 1. As for  $\text{NH}_4^+$  and the peak 4, in drawing 1,  $\text{Li}^+$  and the peak 2 are [ peak 1 /  $\text{Na}^+$  and peak 3 /  $\text{Mg}^{2+}$  and the peak 6 of  $\text{K}^+$  and the peak 5 ]  $\text{Ca}^{2+}$ . In order to show a separation state, the value of  $k'$  ratio of each ion was shown in Table 1. Thus, separation simultaneous good was possible for the univalent and divalent positive ion with sufficient separation width. It was 1.53 meq/g when the ion exchange capacity of this weak acidic cation exchanger was measured with alkalimetry.

[0025]The liquid chromatograph conditions are as follows.

The rate of flow of an eluate: 0.8 ml/min column temperature : 40 \*\* conductivity detector : (trade name: shodex CD-4, Showa Denko K.K. make)

Conductivity :25microS/cmFS [0026]0.16 g of JIKYU mill peroxide was mixed with the comparative example 1 polybutadiene maleic acid 4.0g in a 300-ml eggplant type flask, 150 ml of methanol was added, and it dissolved thoroughly. Next, after adding the silica gel 10g of the particle diameter of 5 micrometers, the pole diameter of 10 nm, and surface area <sup>2</sup>[ of 350 m ]/g and making it suspended uniformly, it condensed making it rotate by 45 \*\* and 650mmHg using a rotating evaporator, and the tunic was formed in the silica gel surface. After silica gel in which the tunic was formed moved only the sieve part opium poppy and the powder portion into the vacuum drier using the sieve made from stainless steel of 200 meshes and made them a nitrogen gas atmosphere, it was heated at 180 \*\* for 4 hours, and manufactured the weak acidic cation exchanger.

[0027]The same sample was measured on the same method as Example 1, and conditions using the obtained weak acidic cation exchanger. The obtained chromatogram was shown in drawing 2. In drawing 2, a peak shows the same substance as Example 1 respectively. In order to show a separation state, the value of  $k'$  ratio of each ion was shown in Table 1. Thus, the univalent positive ion was eluted with narrow separation width, and the divalent positive ion was long late for it, and was eluted. It was 1.21 meq/g when the ion exchange capacity of this weak acidic cation exchanger was measured by the same method as Example 1.

[0028]

[Table 1]

	溶離液	k' 比 (Li <sup>+</sup> を1として)						イオン交換 容量 meq/g
		Li <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	
実施例1)	A	1	1.55	1.93	2.89	4.61	3.79	1.53
	B	1	1.67	2.08	2.98	3.93	5.24	
比較例1)	A	1	1.34	1.54	1.91	5.01	3.66	1.21
	B	1	1.44	1.73	2.24	4.45	5.55	

[0029]It is shown that the polybutadiene maleic acid which ion exchange capacity is large and is a parent of a carboxy group carried out copolymerization bridge construction with high density compared with the comparative example 1, and the weak acidic cation exchanger of Example 1 has covered the silica gel surface from the result of Table 1. The separation width of the positive ion univalent [ eluates / A and B ] in Example 1 has spread, and sufficient separation is performed. Comparing a divalent positive ion relatively to the separation state of a univalent positive ion compared with the comparative example 1, and being early eluted regardless of the eluates A and B was checked. Thus, by the weak acidic cation exchanger of the above-mentioned report which is not so, it was proved to have introduced the hydrophobic group into the weak acidic cation-exchange constituent that an ion exchange action had a big difference. Drawing 1 and drawing 2 are the chromatograms which measured 3mM nitric acid solution as an eluate using the weak acidic cation exchanger respectively manufactured by Example 1 and the comparative example 1.

The above-mentioned thing can judge clearly.

[0030]1.5 g of example 2 maleic anhydrides, and the liquid polybutadiene 1.0g of the average molecular weight 3000, 2,2 and 0.25 g of - azobisisobutyronitrile were mixed with 1.0g of trimethylolpropanetrimethacrylate, and 0.3 g of vinyltoluene in a 300-ml eggplant type flask as a polymerization initiator as a vinyl compound, 150 ml of acetone was added, and it dissolved thoroughly. Next, after adding 10g of silica gel of 25 micrometers, the pole diameter of 50 nm, and surface area <sup>2</sup>[ of 35 m ]/g and making it uniformly suspended from the particle diameter of 15 micrometers, the tunic was formed in concentration and a silica gel surface by 45 \*\* and 650mmHg using the rotating evaporator.

[0031]After carrying out the sieve division of the silica gel in which the tunic was formed, using the sieve made from stainless steel of 200 meshes, moving only the powder portion into the vacuum drier and making it a

nitrogen gas atmosphere, it was heated at 150 °C for 7 hours. 100 ml of sodium bicarbonate solution of 0.2M which contains 20% of methanol after cooling to a room temperature was added, 3 time processings were carried out at 50 °C, and the acid anhydride was hydrolyzed. And it moved on the glass filter of 4G, and suction filtration was carried out. After washing in cold water, 100 ml of 0.5-N hydrochloric acid aqueous solutions washed. Next, 150 ml of water and 150 ml of methanol washed, and the weak acidic cation exchanger was manufactured.

[0032]In this way, the obtained weak acidic cation exchanger is \*\*\*\*(ed) with potassium bromide powder, The place which measured and analyzed the spectrum using simple FT-IR after considering it as a tablet with a tablet molding machine, It became clear from the peak intensity ratio of the absorption band of the carbonyl of the acid anhydride near  $1780\text{-cm}^{-1}$ , and the absorption band of the carbonyl of the carboxy near  $1700\text{-cm}^{-1}$  that 87% is hydrolyzed into the carboxy group.

[0033]The column was filled up with the obtained weak acidic cation exchanger, and the same sample was measured on the same liquid chromatography conditions as Example 1 by making 3mM nitric acid solution into an eluate. this result —  $k'$  of each ion — as for 1.54 and  $\text{K}^+$ ,  $\text{Na}^+$  was [ 1.30 and  $\text{NH}_4^+$  / 2.37 and  $\text{Ca}^{2+}$  of 1.80

and  $\text{Mg}^{2+}$  ] 3.17, when the ratio showed and  $k'$  of  $\text{Li}^+$  was set to 1. Thus, it was possible for elution to have been rash in a divalent positive ion, and to have separated a univalent and divalent positive ion simultaneously. It was 1.25 meq/g when ion exchange capacity was measured by the same method as Example 1.

[0034]The example 3 polybutadiene maleic acid 1.0g and 1.0 g of itaconic acid anhydride, 0.3 g of lauroyl peroxide was mixed with 1.0g of pentaerythritol tetraacrylate, and 2.0 g of styrene in a 300-ml eggplant type flask as a polymerization initiator as a vinyl compound, 150 ml of methanol was added, and it dissolved thoroughly. Subsequently, after adding 10g of silica gel of the particle diameter of 5 micrometers, the pore diameter of 5 nm, and surface area  $^2$ [ of 450 m ]/g and making it suspended uniformly, the tunic was formed in concentration and a silica gel surface by 45 °C and 650mmHg using the rotating evaporator, and the weak acidic cation exchanger was manufactured.

[0035]When spectrum analysis according this weak acidic cation exchanger to simple FT-IR like Example 2 was conducted, the ratio of the carboxy group was 91%. The column was filled up with this weak acidic cation exchanger, and the same sample was measured on the same liquid chromatography conditions as Example 1 by making 3mM nitric acid solution into an eluate. as a result,  $k'$  of each ion — as for 1.53 and  $\text{K}^+$ ,  $\text{Na}^+$  was [ 1.32 and  $\text{NH}_4^+$  / 2.32 and  $\text{Ca}^{2+}$  of 1.85 and  $\text{Mg}^{2+}$  ] 3.23 when a ratio set  $k'$  of  $\text{Li}^+$  to 1. Thus, it was possible for elution to have been rash in a divalent positive ion, and to have separated a univalent and divalent positive ion simultaneously. It was 1.22 meq/g when ion exchange capacity was measured by the same method as Example 1.

[0036]As the example 4 polybutadiene maleic acid 1.75g and a vinyl compound, 0.25g of polyallyl phthalate (thing of the average molecular weight 1000), and 0.25 g of octyl acrylate, 0.15 g of benzoyl peroxide was mixed in a 300-ml eggplant type flask as a polymerization initiator, 100 ml of methanol was added, and it dissolved thoroughly. next, gel permeation, after adding 5.0g of styrene / divinylbenzene gel of [ which are used gruffy / the mean particle diameter of 5 micrometers and 40 nm of average pore sizes ] and making it suspended uniformly, It condensed making it rotate by 45 °C and 650mmHg using a rotating evaporator, and the tunic was formed in styrene / divinylbenzene gel surface. Next, after carrying out the sieve division of the styrene / the divinylbenzene gel in which the tunic was formed, using the sieve made from stainless steel of 200 meshes, moving only the powder portion into the vacuum drier and making it a nitrogen gas atmosphere, it was heated at 150 °C for 6 hours, and manufactured the weak acidic cation-exchange constituent.

[0037]In this way, the column was filled up with the obtained weak acidic cation exchanger, and the same sample was measured on the same liquid chromatography conditions as Example 1 by making 3mM nitric acid solution into an eluate. as a result,  $k'$  of each ion — as for 1.60 and  $\text{K}^+$ ,  $\text{Na}^+$  was [ 1.38 and  $\text{NH}_4^+$  / 2.63 and  $\text{Ca}^{2+}$  of 1.92 and  $\text{Mg}^{2+}$  ] 3.99 when a ratio set  $k'$  of  $\text{Li}^+$  to 1. Thus, it was possible for elution to have been rash in a divalent positive ion, and to have separated a univalent and divalent positive ion simultaneously. It was 1.40 meq/g when ion exchange capacity was measured by the same method as Example 1.

[0038]The silica gel 8.0g used in example 5 Example 1 was taken to a 100-ml Erlenmeyer flask, 70 ml of toluene was added, and it was made to fully get used. Next, it was neglected overnight and vinyl silanizing was carried out, after adding 4 ml of vinyl trichlorosilane, and 1.5 ml of pyridine and sometimes stirring. This silanizing reaction mixture carried out suction filtration with the sintered glass filter of 4G, and reduced pressure drying was carried out at the room temperature after washing with 100 ml of toluene, and 100 ml of methanol. Carbon was 4.24% when ultimate analysis of this silica gel that carried out vinyl silanizing was conducted. The weak acidic cation exchanger was manufactured on the scale of the half of Example 1 using this silanized silica gel.

[0039]The result of having filled up the column and having measured the same sample on the same liquid chromatography conditions as Example 1 by making 3mM nitric acid solution into an eluate after methanol washed the obtained weak acidic cation exchanger,  $k'$  of each ion — as for 2.19 and  $\text{K}^+$ ,  $\text{Na}^+$  was [ 1.75 and  $\text{NH}_4^+$  / 3.99 and  $\text{Ca}^{2+}$  of 3.13 and  $\text{Mg}^{2+}$  ] 5.28 when a ratio set  $k'$  of  $\text{Li}^+$  to 1. Thus, it was possible for elution to have been rash in a divalent positive ion, and to have separated a univalent and divalent positive ion simultaneously. It was 1.59 meq/g when ion exchange capacity was measured by the same method as Example 1.

[0040]The weak acidic cation exchanger was manufactured on the scale of 1 of the half a sum of the comparative example 1 using the silica gel which was compounded in example 6 Example 5 and which carried out vinyl silanizing. When ion exchange capacity was measured by the same method as Example 1, it is 1.51 meq/g and it was proved by carrying out vinyl silanizing of the silica gel that many unsaturated carboxylic acid etc. could be covered with the porous carrier surface.

[0041]0.10 g of benzoyl peroxide was mixed with the example 7 polybutadiene maleic acid 2.0g in a 300-ml eggplant type flask, 100 ml of methanol was added, and it dissolved thoroughly. Next, after adding 5.0g of silica gel used in Example 1 and making it suspended uniformly, it condensed making it rotate by 45 \*\* and 650mmHg using a rotating evaporator, and the tunic was formed in the silica gel surface.

[0042]As one example of a vinyl compound which has an alkyl group of the carbon number 2 in a 100-ml beaker, subsequently, ethyl acrylate, 0.25g of butyl acrylate was respectively taken as one example of propylacrylate and the vinyl compound which similarly has an alkyl group of the carbon number 4 as one example of a vinyl compound which similarly has an alkyl group of the carbon number 3. Subsequently, it weighed 0.25g of trimethylolpropanetrimethacrylate at a time to each, dissolved in 50 ml of pentane, and added to the film formation silica gel prepared three pieces. This was attached to the rotating evaporator, and after carrying out rotation stirring, vacuum concentration was carried out at the room temperature. Stearyl methacrylate which is a vinyl compound in which a carbon number has an alkyl group of 18 is the same mixture ratio as front 3 piece, It dissolved in methanol together with butadiene/maleic acid copolymer, benzoyl peroxide, and trimethylolpropanetrimethacrylate, and covered to silica gel as mentioned above.

[0043]The sieve division of the silica gel which formed the tunic of ion-exchange resin respectively was carried out using the sieve made from stainless steel of 200 meshes, and it moved only the powder portion into the vacuum drier. After nitrogen gas replaced air, it heated at 150 \*\* for 6 hours, and the weak acidic cation exchanger was manufactured.

[0044]After methanol washed these weak acidic cation exchangers, the column was filled up with them and they measured the same sample on the same liquid chromatography conditions as Example 1 by making 3mM nitric acid solution into an eluate. The result was shown in Table 2.

[0045]From Table 2, an ethyl group is presumed to be what most hydrophobic effects do not have, judging from the action of the divalent positive ion of k' ratio. The effect of hydrophobic group with some propyl groups sufficient with a butyl group and a stearyl group in which an effect begins to show up was checked. Ion exchange capacity shows the stable value, and bridge construction by trimethylolpropanetrimethacrylate comes out enough, and it shows a certain thing.

[0046]

[Table 2]

ビニル 化合物の 種類	k'比 (Li <sup>+</sup> を1として)						イオン交換 容量 meq/g
	Li <sup>+</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	
C <sub>2</sub> Ac	1.00	1.57	1.93	2.85	5.87	7.27	1.50
C <sub>3</sub> Ac	1.00	1.53	1.87	2.77	4.47	5.80	1.48
C <sub>4</sub> Ac	1.00	1.60	1.97	2.97	4.07	5.13	1.51
C <sub>18</sub> MA	1.00	1.52	1.90	2.73	3.93	4.93	1.48

注) C<sub>2</sub>Ac: エチルアクリレート

C<sub>3</sub>Ac: プロピルアクリレート

C<sub>4</sub>Ac: ブチルアクリレート

C<sub>18</sub>MA: ステアリルメタクリレート

[Effect of the Invention]Since the weak acidic cation exchanger of the invention in this application is using the polyvinyl compound as a cross linking agent, it is possible for a copolymerization bridging body to cover the porous carrier surface with high density. And manufacture of the packed column which could control that a weak acidic cation-exchange constituent was missing from a porous carrier at the time of column restoration, etc., and was stabilized in liquid chromatography as a result is possible. It is effective in holding sufficient ion exchange capacity to separate a positive ion over a long period of time. Elution of a divalent positive ion can be selectively brought forward by introducing a hydrophobic group into a weak acidic cation-exchange constituent.

[0047]By the two above-mentioned synergistic effects, even if it did not add special reagents, such as pyridine- 2,6-dicarboxylic acid, to an eluate on the occasion of liquid chromatography, it became possible to use common mineral acid, such as nitric acid, as an eluate. Therefore, the use area limited to non suppressor type ion chromatography due to the eluate is expanded also to suppressor type ion chromatography, and it can be expected now that super-minute amount simultaneous analysis of univalent and a divalent positive ion is attained.